

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

0299

The public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments or suggestions for reducing the burden to Department of Defense, Washington Headquarters (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

purposes,
election
Reports
shall be
number.
provision of law, no person shall be
subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE (DD-MM-YYYY) 06-07-2000	2. REPORT TYPE Final Technical	3. DATES COVERED (From - To) 01/06/98 - 31/05/99		
4. TITLE AND SUBTITLE Analytical Equipment for Chemistry Research		5a. CONTRACT NUMBER		
		5b. GRANT NUMBER F49620-98-0464		
		5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Donahue, Edward J.		5d. PROJECT NUMBER 4376/AS		
		5e. TASK NUMBER		
		5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Long Island University/Brooklyn Campus One University Plaza Brookville, NY 11548		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Bolling Air Force Base, DC 20332-0001		10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR		
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				
13. SUPPLEMENTARY NOTES 20010501 080				
14. ABSTRACT This program sought to improve the scientific infrastructure of the Chemistry Dept. of the Brooklyn campus of Long Island University. All of the instrumentation has been used in research by both undergraduate and masters level students. During the grant period eight major pieces of research equipment were ordered, as well as several minor items. There is one publication under review and several more projects are nearing completion, with data being analyzed for inclusion in publications and masters degree theses. The support met the aims of acquiring a broad range of research quality instrumentation for use in chemical research, with an emphasis on the establishment of a capability in the area of materials science.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF: a. REPORT b. ABSTRACT c. THIS PAGE		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON 19b. TELEPHONE NUMBER (Include area code)

Final Technical Report

Grant Number F49620-98-1-0464

"Analytical Equipment for Chemistry Research"

Granted under the

Infrastructure Support Program for Historically Black Colleges/Universities
and Minority Institutions

Submitted by

Edward J. Donahue

Associate Professor, Department of Chemistry
Long Island University

Introduction

This program sought to improve the scientific infrastructure of the Chemistry Department of the Brooklyn Campus of Long Island University. Specifically, its aim was to acquire a broad range of research quality instrumentation for use in chemical research, with an emphasis on the establishment of a capability in the area of materials science. All of the instrumentation has been used in research by both undergraduate and masters level students. There is one publication under review in which the grant is acknowledged. Several more projects are nearing completion, with data being analyzed for inclusion in publications and masters degree theses.

The grant money was expended over the course of one year, starting on 6/01/98 and extending to 8/31/99. During this time, eight major pieces of research equipment were ordered, as well as several minor items. Two points should be noted before a detailed description of the results of the grant are presented. First, from its inception, the grant was designed to be flexible. The original award was funded by the Defense Department at a level of \$269,048. Long Island University matched this with a contribution of \$125,000, of which \$75,000 was to be directly applied towards cost sharing for the major instruments requested and the remaining \$50,000 was to be used to further the aims of the grant by supporting the acquisition of smaller items which, while vital to research, did not fit under the purview of the original Broad Agency Announcement. Secondly, as will be detailed later, there remains approximately \$64,000 encumbered, but not yet disbursed, from the original grant sum. There have been major delays and problems with the installation of a nuclear magnetic resonance (NMR) probe for use with solid samples. These problems are presently being resolved, but the Principal Investigator has withheld payment until installation is satisfactorily completed.

To date, this grant has been acknowledged on two publication:

"Vibrational Spectra of HCl as Studied by Hooke's Law, *ab initio* Calculations, and Experimentally Using FT-IR." Commodari, F., Donahue, E.J., Matsunaga, N. Accepted pending revisions 5/00, *Journal of Chemical Education* in March of 2000.

"Deposition of Crystalline Calcium Hydroxyapatite coatings by Plasma Enhanced Chemical Vapor Deposition." E.J. Donahue, J. Hibbert, Submitted 6/00 to *Journal of Materials Research*

As will be seen, there are many ongoing projects which, upon completion, will duly acknowledge

the support of this grant in all ensuing publications.

Summary of Expenditures:

Instrumentation, Manufacturer, Costs and Order Date and Acceptance Date.

Instrument	Manufacturer	Ordered	Accepted	Cost
Model 7307 Vibrating Sample Magnetometer	Lakeshore Cryotronics	6/18/98	12/07/98	\$124,517
Magna-IR 760 Spectrometer	Nicolet Instruments	6/18/98	10/22/98	\$51,077
DTA7 Thermal Analyzer	Perkin Elmer	6/24/98	10/06/98	\$22,171
LRGAS-300 Mass Spectrometer	Tek-Vac Industries	6/19/98	1/05/99	\$43,090
RS/6000 43P model 150 RS/6000 43P model 260	IBM	8/06/99		\$29,666
*NMR Probe for Solid Samples	Varian	6/18/98	-----	~\$64,000
Upgrade of NMR amplifier	AMT	6/18/98	11/14/99	\$7,750
POWEREX SLP050 Air Compressor	Blackler Air Compressor	7/02/98	9/01/98	\$7,006
X-ray Analysis Software	SIROQUANT	6/23/99	8/27/99	\$4,725
090B Membrane Osmometer	UIC Coulometrics	7/7/98	2/29/99	\$14,235
MET RM180 Rotating Viscometer	Rheometric Scientific	5/19/99	11/03/99	\$7,495
A81030N-LMB GPC Column	Polymer Standards Service	7/19/99	8/31/99	\$1,018
Vacuum Pump	Fisher Scientific		8/27/99	\$2,290
External 40 MB Hard Drives (3)	Microwarehouse	8/02/99	8/17/99	\$1,457
Labworks Software Upgrade	SCI Technologies	7/13/98	9/09/98	\$384
Scanner, Printer (HP)	Compucom, Inc.	8/27/99	10/21/99	\$865
Dell Pentium III PC (2)	Dynamic Decisions	7/13/98	9/09/98	\$1,545
**Fluorescence Spectrometer	PTI Incorporated	6/30/99	8/21/99	\$4,000
			TOTAL	\$387,291

* Funds have not been released for the payment of the Varian NMR probe. The probe has not yet been satisfactorily installed. Details are given in the following section

** Funds were dispersed to supplement and upgrade National Science Foundation Grant NSF-

9975554, which was awarded under the Chemistry Research and Instrumentation Facilities Program. Details appear below.

Detailed Specifications and Summary of Usage for Instrumentation

I. Lakeshore Crytronics Model 7307 Vibrating Sample Magnetometer (VSM):

A) Specifications: Magnetic moment measurements from 1×10^{-6} to 1×10^3 emu, Variable gap electromagnet with applied field range from -14 to +14 kGauss, sweep able. Cryostat and oven attachments allow dynamic temperature dependance measurements from 4K up to 2100K. Windows based software.

B) Usage to Date: The VSM became operational in December of 1998. It has been used in two major research projects to date:

1) Edward J. Donahue: The device was used in the investigation of the formation of yttrium iron garnet, $\text{Y}_3\text{Fe}_5\text{O}_{12}$, (YIG) from a sol-gel technique. Specifically, ethane diol and 1,3 propane diol were used as the solvents in a solution based synthesis using stoichiometric amounts of the hydrated nitrate salts of Y^{3+} and Fe^{3+} . The investigation involved monitoring the transformations which occurred in the samples as they were heated from room temperature to 900°C, the temperature at which the final garnet phase formed. Thermogravimetric analysis (Perkin Elmer TGA7) showed five distinct regions of weight loss in each sample as they were heated up to 900°C. The resulting product of each of these weight losses were examined by X-ray diffraction (XRD-Scintag X-1), FTIR (Nicolet magna 760), differential thermal analysis (Perkin Elmer DTA7), and VSM.

It was found by X-ray diffraction that a low temperature crystalline phase exists below 300°C and the final phase begins to appear above 600°C. These results were confirmed by the VSM measurements, which detected ferromagnetic hysteresis even in the native sol. This hysteresis disappeared above 300°C and reappeared above 600°C. These results indicate that, for each sample, the formation of the sol imparted a definite structural order, giving rise to the ferromagnetic behavior. Magnetic ordering was then lost, along with structural ordering, in the amorphous temperature region. Finally the emergence of the garnet phase was marked by a return of hysteresis. The results gathered from other instruments obtained by this grant will be summarized in the respective sections. Work is presently under way to confirm these initial results. Low temperature studies will be conducted on each sample at every stage of its thermal decomposition. An apparent glass transition, occurring at 30°C, was detected by differential scanning calorimetry (DSC-Perkin Elmer DSC7). This would indicate that a well ordered organo-metallic polymer exists in the sol, a hypothesis supported by room temperature hysteresis detected by the VSM. This DSC work will be repeated using liquid nitrogen as a coolant and magnetic temperature scans will be performed from low temperature on the VSM in an attempt to detect the same glass transition through a change in the magnetic ordering of the sample. High temperature VSM studies will be performed in order to determine the Curie temperature of the final product. If this circumstantial evidence of an organo-metallic polymer is confirmed, efforts will be made to partially determine its properties and structure through osmometry (UIC Coulometrics 090B Membrane Osmometer) and a Electron Paramagnetic Resonance (EPR) Spectroscopy, the latter done in collaboration with the Albert Einstein College of Medicine.

Ms. Nneoma Onukwe, an African-American female, completed her undergraduate research by performing all phases of the initial research. Publications are planned once the initial work is confirmed, with further publications being possible if the presence of an organo-metallic polymer can be substantiated.

2) Adremi Oki: Dr. Oki's research is aimed at the design and synthesis of a series of binuclear transition metal complexes with bridging tetra-oxolene or tetra-amine ligands of the type [(tripod)M-L-M(tripod)]. The L ligands are either derivatives of the dianionic form of 2,5-dihydroxy-1,4benzoquinone or 1,2,4,5 terramino benzene. The tripod ligands investigated are tris(2-benzimidazolylmethyl)amine and its derivatives. These dinuclear complexes, with two redox active metal centers and a bridging ligand whose π^* energy is close to the $d\pi$ of the metal, have allowed us to generate interesting charge distributions. The Lakeshore VSM has been used to determine the magnetic moments of these complexes and, hence, the oxidation states of the metal ions. This project has supported two graduate students, both of whom have used the VSM and the Nicolet FTIR extensively. Ms. Alla Tandalisheva and Mr. Ghassan Abdel-Azziz will be receiving their Masters degrees by the end of the summer and two publications are in preparation which acknowledge DoD support.

II. Nicolet Instruments Magna 760-IR Spectrometer:

A) Specifications: The Magna 760 is a broad band FTIR, capable of obtaining spectra from 25 cm^{-1} up to $11,000\text{ cm}^{-1}$, thereby allowing for the detection of metal containing bonds. An attenuated total reflectance (ATR) attachment was also obtained with the instrument, allowing surface analysis of both thin films and powder/colloidal samples. Use of the far IR capability requires a constant flow of dry air, which is supplied by the Powerex Scroll Compressor.

B) Usage to Date: Needless to say, the mid-range infra-red capabilities of this instrument have been used on a daily basis by all faculty and students, for both research and educational purposes. Only users who have utilized the exceptional near and/or far IR capabilities of the instrument are included in this report.

1) Edward J. Donahue: Doctor Donahue has used the Magna-760 FTIR on three projects.

a) "Deposition of Thin Films of Calcium Hydroxyapatite For Implantable Prostheses." NIH/MBRS program; 3S06-GM54650-021S1. Plasma enhanced chemical vapor deposition (CVD) was used to deposit films of calcium hydroxyapatite (CaP). THE material is meant to be used as an interface for artificial joints, allowing the living bone to join naturally to the implant device. The project is completing its first funding cycle, with reapplication planned for June of 2000. The project involved the synthesis of two classes of organo-calcium compounds, substituted β diketones, and substituted cyclopentadienylides. These volatile organo metalics were successfully used with phosphine to deposit the desired apatite phase from the gas phase on both quartz and titanium metal. Biological compatibility testing is now proceeding and a paper is in preparation which details the deposition of the films.

The far infra-red capabilities of the Nicolet Magna 760 spectrometer were used extensively in this project, as was the ATR attachment. Far infra-red scans were used to confirm the presence

of metals in all organo-metallic compounds by detecting the Ca^{2+} - metal bonds, which typically appeared between 250 cm^{-1} and 380 cm^{-1} , depending upon the organic ligand. The ATR attachment was used, in conjunction with XRD, to characterize the phase and composition of the films produced. This was especially vital to the project, since the combustion of the β -diketone ligands can lead to CaCO_3 impurities which are amorphous to X-ray but show up very strongly in the Infrared spectrum.

Ms. Jacqueline Hibbert, an African American female, performed the work on this grant and is presently preparing her masters thesis based on this project. Mr. Omar Morales, a Hispanic male, also participated in the project by aiding in the synthesis and characterization of the organo-metallic calcium precursors.

b) Sol-gel synthesis of YIG- The particular details of this project are found in the VSM summary above. The far-infrared capabilities of the Nicolet spectrometer were used to monitor the changes in the metal-oxygen bonds as the sol was progressively heated up to 900°C . Of special interest to this project is the fact that the initial sol contained very sharp, easily distinguishable, Fe^{3+} - oxygen and Y^{3+} - oxygen bonds. The position of the bonds, taken in conjunction with VSM, XRD, and DTA data, would indicate that the metal ions form bridges between diolate²⁻ ions, thereby giving a structure to the sol.

c) "Vibrational Spectra of HCl as Studied by Hooke's Law, *ab initio* Calculations, and Experimentally Using FT-IR." Corrected version of manuscript submitted to *The Journal of Chemical Education* in March of 2000. Edward J. Donahue, Nikita Matsunaga, and Fernando Comodari, all of Long Island University, are the authors. This paper, which was favorably received and which has been resubmitted after minor correction, proposes an undergraduate laboratory experiment based upon the venerable experiment using vibration-rotation spectra of HCl. In the submitted paper, the authors propose to have students predict the spectra of HCl, using Hooke's Law approximations, as a pre-lab exercise. Powerful *ab initio* calculations are then performed and the results of both of these calculations are compared to the actual spectrum. The student is then asked to compare each calculational method and, using the spectral data as a reference, determine the limitations and strengths of each method. The Nicolet FTIR was used to obtain the HCl gas phase spectrum. What was of special interest was the spectrometers near-IR capability, which allowed for the actual measurement of the first and second harmonics. Department of Defense support was acknowledged in the submitted manuscript and the experiment is already successfully being employed on campus at LIU.

2) Adremi Oki: Doctor Oki and his students have used the Nicolet FTIR in the above mentioned work with binuclear transition metal complexes with bridging ligands. The near-IR capabilities were used to aid in the determination of the purity of the ligands as they were synthesized. Also, the mid-IR was used to confirm the neutralization of the di-hydroxo-type ligands, with the absence of the -OH stretching band evidencing the creation of the di-anion. The near-IR capabilities were also utilized by Mr. Ghassan Abdel-Azziz in the identification of intervalence charge transfer bands between the metal centers and the ligands.

3) Samuel Watson: Doctor Watson's research activities have made substantial use of the instrument. He and his students have been synthesizing a series of bicyclic lactams designed to

mimic the conformation of a beta-turn. They have used the FTIR extensively to characterize the synthetic intermediates and have also used the instrument to characterize intermediates in a project involving the synthesis of wakayin, an important cytotoxic natural product that exhibits topoisomerase II activity. A third project involving the synthesis of silicon containing anti-folate derivatives as possible anti-tumor agents has also made use of the instrument. At least five different graduate students and two undergraduates have been involved in this work. To date, one publication has arisen out of work done using the instrument.

Talyor, E. C.; Chaudhuri, R. P.; Watson, S. E. "Silicon-Containing Antifolates", *Tetrahedron* 1999, 55, 1631.

III. Perkin Elmer DTA7 Differential Thermal Analyzer

A) Specifications Differential thermal analyzer with temperature range from room temperature up to 1200°C. Purchase also included software upgrade to Windows compatible Pyris software. This purchase complements the Perkin Elmer TGA7 and DSC7, which the department already owned. The new software allows for simultaneous data acquisition from all three systems.

B) Usage to Date: Doctor Edward Donahue has used the DTA extensively in his work on sol-gel YIG. The instrument was used in conjunction with thermal-gravimetric analysis to monitor the decomposition of the sol as it was heated and transformed into the final ceramic garnet. Interestingly, the DTA detected exotherms corresponding to each weight loss step in the decomposition of the sol. Endotherms were detected at temperatures in excess of 800°C, indicating crystallization. Interestingly, these endotherms were not sharp, and X-ray analysis indicated the presence of a weakly crystalline garnet phase above 500°C. This evidence lends further credence to the theory that the sol-gel preparation imparts a definite structure to the material, allowing it to crystallize at lower temperature and at much less energy than is seen in conventional solid state preparations. Also, the longer chain propane diol sols seemed to consistently crystallize at temperatures approximately 75°C lower than sols prepared from ethane diol. This would seem to indicate that the longer hydrocarbon chain gives the organo-metallic polymer greater freedom to arrange itself in an energetically favorable conformation. DTA analysis will be crucial to the continuation of this project over the coming summer, where all syntheses and experiments will be repeated and, as mentioned above, further testing will be performed.

IV. Tek-Vac Industries LRGAS 300 Residual Gas Analyzer (RGA)

A) Specifications: THE LRGAS 300 is a portable mass spectrometer with a range of 0-300 amu. Resolution of +/- 1 amu is achieved through the use of nine quadrupoles. The mass spectrometer head and electronics are produced by Ferran Scientific, San Diego, CA. The system is modular, with the head and electronics package attached to flexible stainless steel vacuum line. The system is evacuated by means of a turbo molecular pump, achieving a base pressure of 10⁻⁸ Torr. The use of a metering valve on the mass spec inlet allows for the sampling of gases at atmospheric pressure. The Mass spec can function at a pressure of up to 1 millitorr beyond the metering valve and has automatic high pressure shut down capabilities to protect the filaments.

B) Usage to Date: The RGA has been used extensively in Dr. Donahue's NIH funded project on the chemical vapor deposition of calcium hydroxy apatite. The mass spec head is configured so that it sits at the end of an o-ring sealed flange, which can be directly mounted on the CVD reactor.

Samples are taken from both the inlet side of the reactor and near the pumping port, with comparison of the mass spectrum giving an indication of the reaction occurring within the reactor. For example, it was found that the use of β -diketone type precursors produces carbon dioxide and water on the downstream side, with no detectable hydrocarbon residue. THIS is proof of the fact that these ligands are not good leaving groups, but rather must completely combust before releasing the calcium ion into the reaction. Preliminary tests using calcium bis(cyclopentadiene) have shown just the opposite effect, with sharp mass spectrum peaks occurring at 65 amu, indicative of the ligand leaving the reactor intact after the reaction. This is an important discovery, since the presence of elevated amounts of CO₂ caused by combustion lead to the formation of undesirable calcium carbonate impurities in the final films.

V. IBM RS/6000 43P, models 150 and 260

A) Specifications: Two work station IBM computers were purchased in lieu of the SILICON Graphics work station originally requested. The department purchased a Silicon Graphics machine subsequent to the submission of the grant application. While it was felt that improvements in the computational capabilities of the department were still required, it was decided that the graphics capabilities of the SI machine did not need to be duplicated. Therefore, the two IBM machines were chosen. Each machine runs on two paralleled RS 6000 processors and the machines can also be paralleled with each other and with the SGI. The model 150 came with 512 Mb of memory while the model 260 was equipped with 1 Gb of memory. THE limited memory was the trade off in receiving an excellent discount of nearly 50% on the purchase. This allowed us to fully upgrade these machines and the SGI through the purchase of three 10 Mb Maxtor external hard drives for only \$1,500.

B) Usage to Date: Doctor Nikita Matsunaga has been the primary user of these machines. His research since last fall has utilized both machines heavily. He has indicated that, without such resource, he could not have accomplished as much as he did during the past two semesters.

1) One of the projects deals with elucidation of stability of various O-nitrenes, which is considered to be an important reactive intermediates in the photodissociation of photoprotected diazeniumdiolates. The diazeniumdiolate is known to show cytotoxic activity toward tumor cells. The experimental part of this collaborative project is carried out in the laboratories of Prof. John P. Toscano at The Johns Hopkins University, and the theoretical calculations are carried out by Dr. Matsunaga at LIU.

2) Another project that has benefitted, involves elucidation of mechanism of NO scission process with M(OR)₃, where M = V, Nb, and Ta. The experimental collaboration is done with Prof. Peter Wolczski at Cornell University and the theoretical calculation has been performed with Prof. Thomas Cundari's lab at Univ. of Memphis and Dr. Matsunaga's group at LIU. Doctor Matsunaga has demonstrated importance of triplet state in explaining the mechanism of the scission process. In order to improve prediction of vibrational frequencies in the electronic structure theory, Dr. Matsunaga has been coding a new theoretical treatment, called vibrational self-consistent field (VSCF) approach and one of his students, Mr. William Howard (African American, M.S. degree

expected in Spring, 2001), has been examining the effect of solvation in small molecules as applied to the VSCF.

VI. Cross-Polarization/Magic Angle Spinning (CPMAS) NMR Probe for Solid Samples-Varian

Original order was placed for a Chemagnetics Double Resonance 400NB probe with HX filter. This order was placed on 6/18/98 with an expected shipment time of eight months. After one year, the vendor admitted that the probe in question was actually only an experimental design which was still not perfected. The university was given a choice of waiting another year or replacing the probe with a slightly less capable standard 5 mm CPMAS probe. The university chose the second option, at a cost savings of \$6,200.

The replacement probe was shipped and received in December of 1999. However, upon attempted installation, it was found that the spin was not properly controlled and that furthermore, the high power upgrade (item VI) had caused several problems with the spectrometer electronics. At present, the spectrometer has been completely checked out and we are awaiting the return of the probe, which was sent back to the vendor in order to re-regulate its spinning. Payment has been withheld until the probe has been successfully installed and has met specifications.

VII. AMT Corporation: Upgrade of NMR Amplifier:

A) Specifications: The Varian INOVA 400 MHz NMR presently on campus is equipped with a two channel amplifier, Model number 3900-12. In its original configuration, channel 1 had a power output of 50 watts and channel 2 had an output of 300 watts. As part of the CPMAS probe purchase, channel 1 was upgraded to 300 watts. The upgrade was successful, with both amplifiers meeting specifications.

B) Usage to Date: Due to the problems enumerated in V, this amplifier has only been used in routine, qualitative, proton NMR experiments.

VIII. Air Compressor/Dry Train System (Contractor: Blackler Air Compressors, Brooklyn, NY)

A) Specifications: The system, which was installed in September of 1998, consists of a Powerex SLP05, 5 HP compressor. This unit is an oil less scroll compressor housed in a sound proofed enclosure. The compressor delivers up to 14 cubic feet of air per minute at 110 PSIG. The air is then passed through a self regenerating Deltech zeolite desiccant system and a Deltech particulate filter. Finally, the air is passed through a Deltech HX series refrigerated dryer, producing clean air with a tested dew point of -140°C. The air is then sent to an 80 gallon holding tank.

B) Usage to Date: The system, which was originally purchased to provide a reliable source of dry air to the NMR and the Nicolet FTIR, has performed flawlessly. It is now used to supply compressed air to all instruments in the centralized instrumentation facility, replacing a total of 8 compressed air bottles which were previously in constant usage. The compressor has been in operation for nearly two years and, except for maintenance, has never been off-line. The large pumping capacity enables the compressor to operate at a quite leisurely 30% duty cycle.

This completes the list of equipment specifically mentioned in the original grant application. The following items were purchased as part of Long Island University's matching effort, with an aim towards establishing a strong capability in materials Science, both inorganic and polymeric

IX. SIROQUANT X-Ray Analysis Software

X. Gonotec OSMOTAT 090B Membrane Osmometer (UIC Coulometrics (Joliet) Distributor)

A) Specifications: Automatic membrane osmometer, capable of measurement of molecular weights from 10,000 up to 2,000,000 daltons by means of interchangeable membranes. Thermostated to +/- 0.1°C, the measurement cell temperature can be regulated from 30°C up to 130°C. Stainless steel/Teflon/glass construction allows sampling in all organic solvents Minimum detectable pressure deviation is 0.1 mm Hg.

B) Usage to Date: Doctor Hannia Luján-Upton is the primary user of this device. She is a polymer specialist and through the graduation of five masters students over the past four years, she has been instrumental in the establishment of polymer science at the Brooklyn center of LIU. Doctors Edward J. Donahue and Azzedine Bensalem also plan on using the osmometer in the near future in order to determine molecular weights of organo-metallic sol-gel type polymers.

Doctor Hannia Luján-Upton is presently investigating the gelling mechanism of 2-hydroxyethyl methacrylate (HEMA), a material widely used in a variety of biomedical implants. The pure material is difficult to manufacture due to its tendency to instantaneously cross-link, creating an insoluble gel. Two hypotheses are presented for this behavior. The first was that ethylene glycol dimethacrylate (EGDMA) was responsible for the cross linking. This chemical is an unavoidable contaminant in the HEMA monomer and is a cross linking agent. The second hypothesis is that the hydroxyl group on the monomer provides a site for an elimination reaction between chains, causing cross-linking.

Initial investigations proceeded upon two paths. Firstly, a monomer was synthesized wherein the hydroxyl group was protected with a silyl group. This produced a readily soluble polymer which cross linked upon deprotection. Secondly, ultra-pure HEMA monomer was prepared in which EGDMA was eliminated, as determined by gas chromatography. Soluble, non-cross linked material was obtained in this case also, even though the hydroxyl groups were not protected.

The results of this preliminary work was therefore inconclusive. Research is presently ongoing in order to clarify the situation through studying the rate of cross linking under various temperatures and conditions, as well as the rate as a function of polymer weight. The membrane osmometer is vital to this second phase, as it allows exact determination of rate constants through accurate measurement of molecular weights. Also, since the membrane osmometer is a direct method of measurement, it will allow for the determination of the molecular weights of HEMA copolymers, many of which are poorly characterized and therefore do not have reliable Mark-Houwink constants associated with them.

XI. Rheometric Model RM180 Rotating Cone Viscometer

A) Specifications: Allows for both single point measurement and automatic flow curve calculation. Automatically calculates both dynamic and kinematic viscosity, as well as shear rate, shear stress and torque. Allows variable temperature sampling for kinetic experiments and is capable of measuring viscosities in a range from 1 to 10^6 mPa-s. Allows for the viscosity measurement of non-flowing gel like materials. Computer interfacable.

B) Usage to Date: Presently being used by Professor Luján-Upton in order to measure the cross-linking kinetics of various HEMA co-polymers. In conjunction with the membrane osmometer, this device is being used to perform a matrix of experiments concerning molecular weight versus temperature versus time versus percent cross linking. The rotating cone method allows for the measurement of viscosities up to and including the final degree of cross linking, a point well beyond that which the polymer solution would flow through a conventional time of flight viscometer.

Doctor Donahue will use the device in the coming summer in order as part of his investigation of ferromagnetic YIG sols and gels. The intrinsic viscosities of the native sols and the subsequent gels will be measured, and using information from the membrane osmometer, Mark-Houwink constants will be determined. It will be determined if there is a conventional relationship between molecular weight and viscosity, or whether the presence of magnetic ordering affects the viscosity of the sol. Experiments will be performed in the presence of a magnetic field in order to support any conclusions. Also, as a reference, sols and gels of the non-magnetic yttrium aluminum garnet will be synthesized, measured and compared to YIG.

XIII. Polymer Standards Services GPC Column (model A81030N-LMB

A) Specifications: Gel permeation chromatography column for use with Hewlett Packard model 1050 High Pressure Liquid Chromatograph. Includes a set of five reference standards. Capable of separation of high molecular weight polymers ranging in size from 10,000 daltons to 2,000,000 daltons.

B) Usage to Date. Used as both a preparative and analytical tool. Doctor Luján-Upton has been the primary user, utilizing the column to determine the dispersity of synthesized poly HEMA and c-poly HEMA molecules. The column will be used as a preparative tool in conjunction with the membrane osmometer and the rotating cone viscometer, allowing for the measurement of nearly mono-disperse polymeric materials.

XIV Mechanical Vacuum Pump - Sargent Welch

A) Specifications: Standard two stage mechanical vacuum pump, capable of 10^{-3} torr base pressures at a pumping rate of eight liters per minute.

B) Usage to Date: Purchased for use with the cryostatic attachment for the vibrating sample magnetometer. Stainless steel Dewar must be evacuated and backfilled with liquid helium several times in order to maintain proper operation. Also. The high temperature furnace for the same device

must be evacuated in order to prevent losses by convection and conduction, which could overload the small heating elements.

XV External Hard Drives (3)

A) Specifications: 40 MB external hard drives with SCSSI ports.

B) Usage to Date: Purchased in order to increase the capability of the IBM work station purchased under this grant, as well as the SGI workstation already present in the department. Cost of external drives as an add-on to these systems was more economical than buying large hard drives as original equipment.

XVI Labworks™ Software Upgrade

A) Specifications: Labworks is a general purpose computer interface system which allows for computer control of instruments through an RS 232 interface box.

B) Usage to Date: Labworks allows for the automatic gathering and interpretation of various titration and spectroscopic data. The system has been in use both in teaching and research laboratories for three years. The upgrade made the software Windows compatible. Older version operated in DOS

XVII Dell Pentium III PC's (2)

A) Specifications: 300 MHz, 2 Gb hard drive, 128 Mb RAM, Pentium III processor.

B) Usage to Date: Purchased in order to upgrade instruments. One PC is dedicated to the Perkin Elmer thermal analysis equipment. A software upgrade for the entire system was purchased along with the differential thermal analyzer. The old system was UNIX based, the new system is Windows based. The second PC was used for a similar upgrade to the Perkin Elmer Lambda II UV-visible spectrometer. In this case, a second parallel port was added so that the UV and the fluorescence machine (see XVIII) could share the same platform.

XVIII Photon Technology Industries (PTI) Fluorescence Spectrometer

Ten thousand dollars from this grant was used to supplement National Science Foundation Grant NSF-9975554, allowing for the purchase of a more capable fluorescence spectrometer

A) Specification: The PTI system is modular, with a central sample chamber capable of accepting up to four detectors and emitters. As configured, the system is capable of scanning fluorescence measurements of both excitation and emission. It is also equipped with a Xenon flash lamp and gated detectors for performing static lifetime measurements down to the pico-second range. This machine is an improvement on the device originally requested in the NSF grant applications in that the original device was only capable of lifetime measurements down to the micro-second range.

B) Usage to Date: To date, Dr. Hannia Luján-Upton has been the primary user of the machine. Her research focuses on using fluorescent probes such as Tb^{3+} to determine the local chelation environment in tactic polymers. Such polymers are used as models of more complex biological macromolecules